669.8
W682s
v.2

U.IV[illegible]ITY OF ILLINOIS
URBANA, ILLINOIS

[illegible] ROOM

FUNDAMENTAL STUDY OF PROPERTIES OF REFRACTORIES AS RELATED TO SERVICE IN A STEEL PRESSURE CASTING PROCESS

SPONSOR
GRIFFIN WHEEL COMPANY
CHICAGO, ILLINOIS

FEBRUARY 1, 1961

DEPARTMENT OF CERAMIC ENGINEERING

UNIVERSITY OF ILLINOIS

URBANA, ILLINOIS

THE LIBRARY OF THE
MAR 6 1961
UNIVERSITY OF ILLINOIS

SECOND SUMMARY REPORT

ON

FUNDAMENTAL STUDY OF PROPERTIES OF REFRACTORIES AS RELATED TO SERVICE IN A STEEL PRESSURE CASTING PROCESS

SPONSOR
GRIFFIN WHEEL COMPANY
CHICAGO, ILLINOIS

FEBRUARY 1, 1961

by

T. A. Willmore, P. D. Zimmerman, J. M. Bearden,
A. W. Allen

DEPARTMENT OF CERAMIC ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

FOREWORD

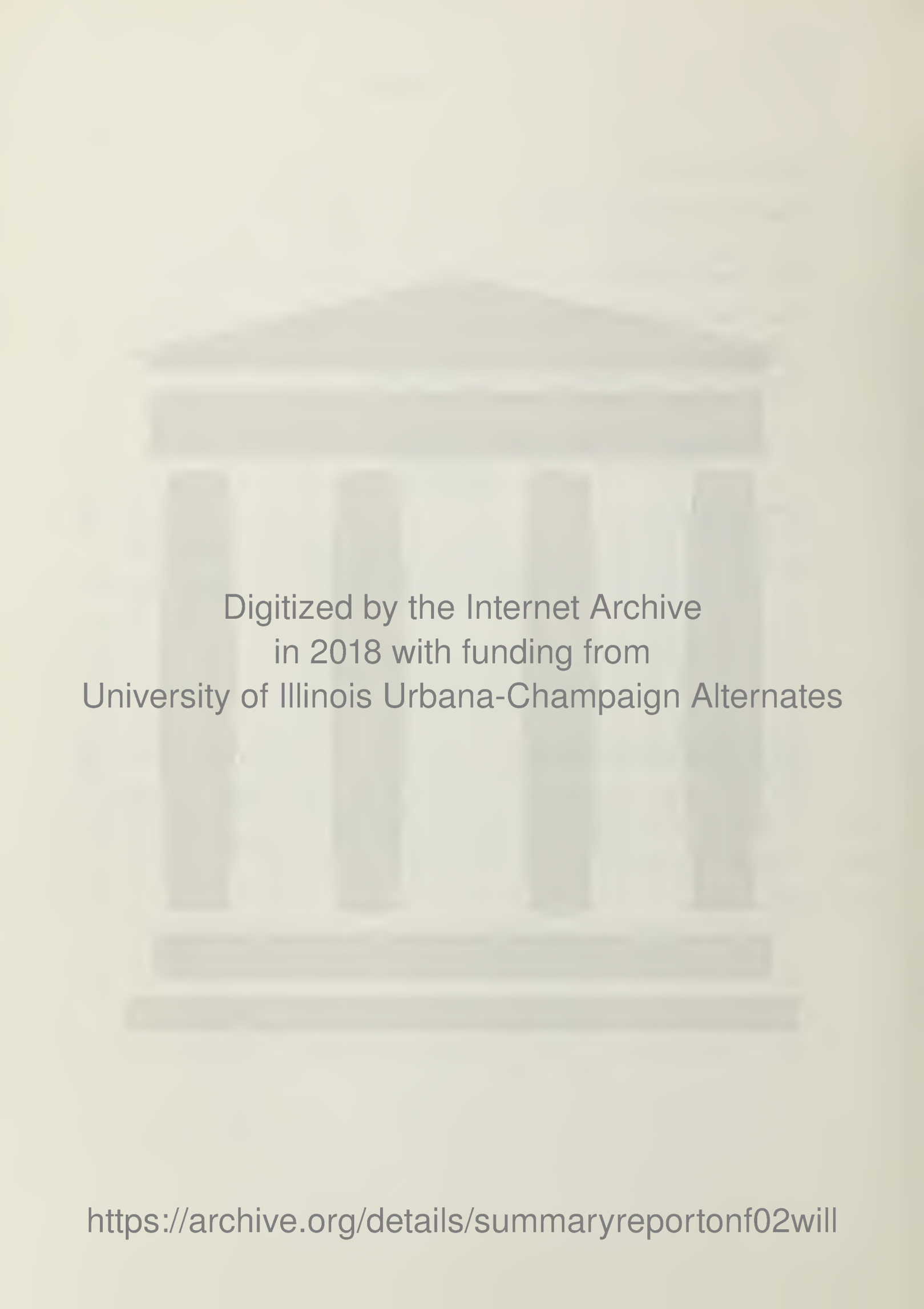
This report summarizes the work done between February 1, 1960 and January 31, 1961 under a continuation of the co-operative research project sponsored by the Griffin Wheel Company in the Department of Ceramic Engineering at the University of Illinois. It contains information related in Interim Reports Nos. 13, 14 and 15, issued between May 6 and November 9, 1960; also included are additional data obtained between November 1, 1960 and January 31, 1961.

669.8
W682
v.2

Empiu

Table of Contents

		Page
I.	Introduction	1
II.	Simulated Service Tests	2
	Tube Fabrication	2
	Dip Test Results	4
III.	New Body Compositions	8
	Materials	8
	Properties of Magnesial-Spinel and Zirconia-Spinel Compositions	9
IV.	Properties of Fused Spinel Bodies as Affected by Heat Treatment	15
	Compositions	15
	Fired Properties	16
V.	Effect of Particle Size Distribution on the Properties of Fused Spinel Bodies	23
	Compositions	23
	Fired Properties	26
VI.	Ring Section Deformation Studies	32
	Introduction	32
	Apparatus and Procedure	35
	Results	36
VII.	Aluminum Titanate	39
VIII.	Service Projects	41
IX.	References	43


Digitized by the Internet Archive
in 2018 with funding from
University of Illinois Urbana-Champaign Alternates

https://archive.org/details/summaryreportonf02will

List of Tables

Table		Page
1.	Fused Spinel Bodies in which GE Grade 12750 Fused Periclase was Substituted in the Fine and Intermediate Fractions	10
2.	Fused Spinel Bodies in which Zircoa Magnesia-Stabilized Fused Zirconium Oxide was Substituted in the Fine Fraction	11
3.	Physical Properties of Experimental Fused Spinel Bodies Containing Fused Periclase or Magnesia-Stabilized Zirconium Oxide as Fired at 2700°F. for Five Hours and After Reheating at 2910°F.	13
4.	Iron Oxide Bursting Characteristics of Fused Spinel Bodies Bearing Either Fused Periclase or Magnesia-Stabilized Zirconia	14
5.	The Effect of Time and Temperature on the Fired Properties of Fused Spinel Bodies O-F4 and MO-5F4 . .	17
6.	Variations of Bodies O-F5 (100% Fused Spinel) and MO-5F5 (5% Magnesium Oxychloride) Used to Study the Effect of Particle Size Distribution on the Physical Properties	25
7.	Physical Properties of Fused Spinel Bodies Used in the Study of the Effect of Particle Size Distribution (Firing conditions: 5 hr. at 2800°F. . .	27
8.	Percent Deformation as Function of Time and Temperature for Samples A and C	37
9.	Percent Deformation as a Function of Time and Temperature for Samples B and D	38

List of Figures

Figure		Page
1.	Dip Tested Tubes	5
2.	Permeability Apparatus	19
3.	The Effect of Firing Time and Temperature on the Apparent Permeability of Body O-F4	21
4.	The Effect of Firing Time and Temperature on the Apparent Permeability of Body MO-5F4	22
5.	Apparent Permeabilities of Modifications of Body O-F5	30
6.	Apparent Permeabilities of Modifications of Body MO-5F5	31

ABSTRACT

Several simulated service tests were made, and the resistance of spinel refractories to erosion by molten wheel steel has been demonstrated. A comparison between polyvinyl alcohol and a water-soluble wax as temporary binders for ramming mixes has shown the wax to be more effective in producing high densities.

The fired properties of fused periclase-magnesium aluminate and fused zirconia-magnesium aluminate composites have been determined. The substitution of either oxide for a portion of the fused spinel had detrimental effects on the room temperature strength.

The effects of firing time and temperature and also of the particle size gradation on the physical properties of fused spinel bodies have been studied. All three may be varied widely without much change occurring in any room temperature properties except permeability.

An apparatus to study the deformation of ring sections while they were subjected to both heat and load has been constructed. Some preliminary results have been presented.

Probing experiments with fused aluminum titanate have been described.

A number of service projects, completed at the request of the Sponsor, have been enumerated.

I. INTRODUCTION

The initial Summary Report related to this subject was issued February 1, 1960. It contained an account of detailed studies of a number of refractory compositions composed preponderantly of sintered or fused magnesium aluminate grain. Such work is related to the development of new refractories for use in the steel pressure pouring process.

Factors investigated included: (1) modifications in composition through the addition of minor amounts of auxiliary ceramic materials and their effect on the fired properties, including resistance to iron oxide bursting; (2) a study of forming procedures whereby small tubular specimens could be fabricated; and (3) the effect of particle size distribution in the fine fraction on the fired properties.

As a corollary endeavor, an automated apparatus to evaluate the erosion and corrosion of refractories while in contact with molten steel was constructed, and a procedure perfected by means of which tubular specimens could be cycled into the steel. Such a procedure was anticipated to be useful as a simulated service test for many kinds of refractories. Most of the work items were designed to produce information which would specifically help commercial refractory manufacturers to produce full size pouring tubes for plant trials by the Griffin Wheel Company.

Fused spinel was used almost exclusively inasmuch as this was being produced commercially at the outset of the investigation, whereas sintered spinel was not. The concentration on this type of grain was again done deliberately to expedite early

plant trials. Three different lots of fused spinel were used. These are differentiated by the designations F3, F4 and F5 in the various body numbers. All were supplied by the Muscle Shoals Electrochemical Corporation and differed mainly in the particle size gradation of the fine fraction.

Reference to the Summary Report for 1960 will supply specific detailed information relative to tube fabrication, mixing processes, physical property determinations, etc.

II. SIMULATED SERVICE TESTS

Tube Fabrication

A small scale pouring tube having the dimensions 3-in. OD by 1½-in. ID and with a nominal length of 25 inches is required for the simulated service test. Ramming these appeared to be the most practical way of forming such specimens, and a technique to do this was worked out.

Two troublesome features developed. Wax bonded bodies were exceedingly fragile and, therefore, difficult to handle. The presence of magnesium oxychloride in the mix often caused sticking to the mold walls and subsequent surface tearing when the piece was stripped.

Using Body O-F3 (100% fused spinel), a comparison was made of the relative effectiveness of polyvinyl alcohol (PVA) and Carbowax 4000 as temporary binders. The grain sizing in this body was: coarse - 45%, intermediate - 15% and fine - 40%.

A low viscosity PVA, DuPont's Elvanol 70-05, was used.

This, due to its slow solubility in cold water, had to be added as a solution. Since maximum possible solution strength for this grade is around 30%, in order to get an effective amount of solids (1½ to 2½%) into the mix, more water had to be added than was compatible with a ramming mix. In "drying back" to a ramming consistency, the PVA hardened to a degree which impaired flow.

The relatively poor lubricating characteristics of the PVA when compared to 1½% Carbowax 4000 dissolved in water became apparent when the fired densities of some of the tubes were determined. For example, PVA-bonded tubes, after being fired for 5 hours at 2910°F., had densities in the range 2.55 to 2.74 g/cc. Wax-bonded tubes of the same O-F3 composition fired under identical conditions had densities in the range 2.8 to 2.86 g/cc. The normal fired density for this body as determined from dry pressed, wax-bonded bars is about 2.89 g/cc.

PVA, although it produced unfired tubes which were much stronger and easier to handle, was not, therefore, considered to be as effective a temporary binder as Carbowax 4000.

Two tubes containing 2½% PVA were rammed of Body MA-15F3; 15% spinel formed in situ from the component oxides is the bond in this body. The mix rammed well, and the pieces formed were hard and strong. After firing at 2910°F., both tubes had developed fine peripheral cracks at the mid-section. These extended about one-third the distance around the circumference. Uneven support by the bedding material in the kiln rather than incipient defects due to forming probably caused this since

both tubes cracked on the under side. No densities were measured because of these defects.

Five tubes of Body MO-5F3 (the bond in this body was 5% MgO plus 3.85 % of 1.2 g/cc solution of $MgCl_2 \cdot 6H_2O$) were rammed to determine some way of preventing the tubes from bonding to the mold wall when the magnesium oxychloride "set". Light oil, heavy oil and painted-on paraffin coatings did not prevent sticking. This problem was solved through the application of a light coating of a spray-on plastic ("Spray-Fix") on the inner surfaces. This particular body had excellent ramming characteristics. The fired densities of the tubes ranged from 2.9 to 2.95 g/cc. Dry pressed specimens of the same mix had fired densities of about 2.85 g/cc.

Dip Test Results

A tube composed of Body MO-5F3 was cycled into molten wheel steel for a total immersion time of 50 minutes. At the completion of the final immersion, the tube was abruptly withdrawn from the furnace. The net effect of this thermal shock was the development of one 2-inch longitudinal crack which extended to the extreme lower end of the tube.

Examination of this tube at the ends of the test showed very little attack by the steel. Figure 1 shows the dipped end of this tube and that of a small alumino-silicate tube, which was tested under identical conditions.

In spite of a small mid-line crack which had developed during firing, one of the MA-15F3 tubes was dip tested. This

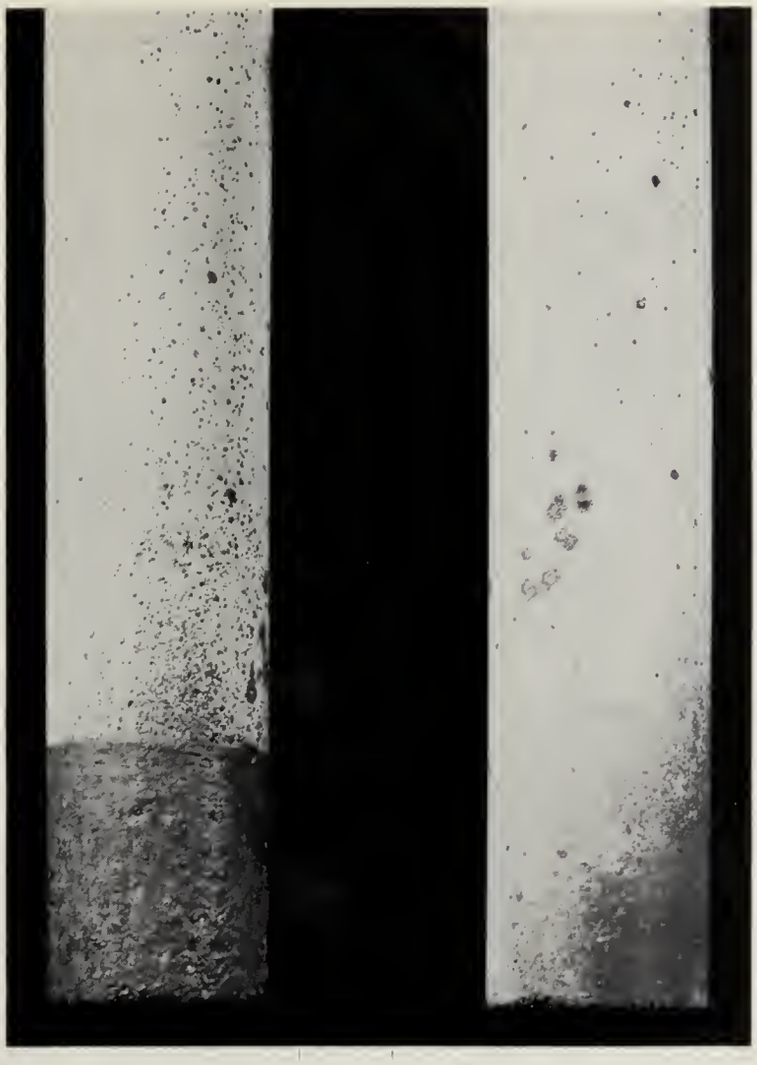


Fig. 1. Lower Ends of Alumino-Silicate (left) and MO-5F3 Tubes after Simulated Service Test. Total immersion time for each was 50 minutes.

tube was cycled in and out of molten wheel steel (2850°F.) 10 times on a 6-minute immersion and 2-minute withdrawal schedule. At the end of the test, the tube was withdrawn from the furnace without failing in thermal shock.

Structural alteration was more apparent in this tube. The surface had changed to a light yellow color where exposed to the steel. Localized slagged areas were also noted at the outer edge of the lower end. These were not thought to be due to attack by the steel or iron oxide but rather from acid slag created by pieces of insulating brick which fell from the furnace top into the crucible.

One tube of Body O-F3 was also tested. However, in this case, the tube was preheated in an auxiliary furnace and then transferred to the dip test facility. Although the tube was suspended just above the steel for 15 minutes before it was immersed, apparently the tube was sufficiently cold to chill the steel on the top surface. The force of the hydraulic ram then caused the tube to break off about 11 inches from the lower end. This broken end was deliberately left in the molten steel continuously for 90 minutes but due to restricted space could not be extracted from the furnace as planned. Therefore, the tube, still immersed, was allowed to cool with the steel. Only a very slight reaction zone was evident in the refractory when the cooled composite was examined. This particular tube had been formed with PVA as a temporary bond and, it should be recalled, such tubes had lower densities than is normal for this composition.

III. NEW BODY COMPOSITIONS

Materials

Since it was desired to study the influence of fused magnesia and fused zirconia on the properties of bodies which are predominantly fused spinel, two series of bodies were formulated in which these materials were substituted for fractions of the magnesium aluminate.

The fused magnesia was obtained from the General Electric Company. It is identified as No. 12750 high purity, refractory grade periclase and has the following typical analysis:

	%
MgO	99.2
SiO_2	0.5
CaO	0.1
Fe_2O_3	0.1
Al_2O_3	0.1

The magnesia-stabilized, fused zirconia was supplied by the Zirconium Corporation of America. This is somewhat a special product inasmuch as lime-stabilized ZrO_2 is much more commonplace. While no analysis was supplied, the following (which was deduced from analyses of their other grades of stabilized zirconia) is probably a close approximation:

	%
ZrO_2	92.5 (includes HfO_2)
SiO_2	0.4
CaO	0.2
MgO	5.6
Fe_2O_3	0.2
Al_2O_3	0.5
TiO_2	0.5

The fused spinel was designated as Lot F4 since the particle size distribution of the fine (-65 mesh) fraction varied somewhat from the lots used in previous work. All bodies containing this particular grind are identified by the F4 designation in the body number. This convention will be recognized as that previously adopted to help differentiate between bodies which varied only in the particle size gradation of the fine fraction.

Properties of Magnesia-Spinel and Zirconia-Spinel Compositions

The bodies formulated are shown in Tables 1 and 2. To produce magnesia or zirconia-rich matrixes, the oxides were substituted in 10% increments for the fine fraction of fused spinel until this had been entirely replaced. Magnesia, in corresponding particle size, was also used to replace the intermediate size fraction in one body, thus producing a composite with 55% MgO and 45% $MgAl_2O_4$. Body O-F4 (100% fused spinel) was included to furnish comparative data.

The particle size gradations of the -65 mesh fused oxides did not precisely match that of the spinel which they replaced. The variations in particle sizing are shown in footnotes in Tables 1 and 2.

These bodies were processed as follows: 20 1-in. x 6-in. bars and two 1¼-in. diameter cylinders were pressed at 7500 psi, using 3% Carbowax 4000 (dissolved in 1.4% water) as a binder. All bars and cylinders were fired for 5 hours at 2700°F. and 10 bars and 1 cylinder were reheated at 2910°F. The resistance of these bodies to iron oxide bursting was determined by the

Table 1

Fused Spinel Bodies in which GE Grade 12750 Fused Periclase was Substituted in the Fine and Intermediate Fractions

	Per Cent by Weight				
	Spinel Grain			Periclase Grain	
Body No.	-8 +20 mesh	-20 +65 mesh	-65* mesh	-20 +65 mesh	-65** mesh
O-F4	45	15	40	--	--
P1-F4	45	15	30	--	10
P2-F4	45	15	20	--	20
P3-F4	45	15	10	--	30
P4-F4	45	15	--	--	40
P5-F4	45	--	--	15	40

*Particle Size		**Particle Size	
-65 +100	9.3%	-65 +100	10.7%
-100 +200	7.8%	-100 +200	13.5%
-200 +270	10.9%	-200 +270	7.9%
-270	71.8%	-270	67.9%

Table 2

Fused Spinel Bodies in which Zircoa Magnesia-Stabilized Fused Zirconium Oxide was Substituted in the Fine Fraction

	Per Cent by Weight			
	Fused Spinel			ZrO_2**
Body No.	-8 +20 mesh	-20 +65 mesh	-65* mesh	-65 mesh
ZM1-F4	45	15	30	10
ZM2-F4	45	15	20	20
ZM3-F4	45	15	10	30
ZM4-F4	45	15	--	40

*Particle size gradation given in footnote of Table 1.

**Particle Size

-65 +100	10.4%
-100 +200	15.7%
-200 +270	10.5%
-270	63.4%

procedure outlined in the 1960 Summary Report. Other physical property data were obtained by conventional procedures.

The physical property data obtained from these tests are summarized in Tables 3 and 4. The use of both oxides had a deleterious effect on the room temperature strength. The MgO-bearing bodies became progressively weaker as the amount used increased. With ZrO_2 the strength decreased to a minimum and then increased slightly, but did not recover to the strength of the body without the additive.

Fused magnesia had little influence on the other physical properties measured until it was present in amounts of 40 or 55%. A sharp, but by no means excessive, change in the firing expansion was noted in these cases. Successive increases in the ZrO_2 content of the bodies caused increases in the porosity and bulk density. The density change, of course, is due to the replacement of a lighter material by a heavier one.

Only the fused periclase enhanced the iron oxide bursting resistance. However, this required 20% or more of the oxide. An attendant effect was the reduction in room temperature strength to a level which is considered unsatisfactory (modulus of rupture below approximately 900-1000 psi).

On the basis of the properties measured, it can be concluded that, as used, neither fused MgO nor fused ZrO_2 are particularly effective in improving spinel-base bodies. However, the presence of these oxides at elevated temperatures may be beneficial. This would have to be determined by additional tests.

The fired properties of the control body, O-F4, compare

Table 3

Physical Properties of Experimental Fused Spinel Bodies Containing Fused Periclase or Magnesia-Stabilized Zirconium Oxide as Fired at 2700°F. for Five Hours and After Reheating at 2910°F.

Body No.	Apparent Porosity, %		Bulk Density, g/cc		Linear Change, % (1)		Modulus of Rupture, psi		Youngs Modulus psi (x 10^{-6})	
	2700°	2910°	2700°	2910°	2700°	2910°	2700°	2910°	2700°	2910°
O-F4	21.4	20.7	2.79	2.81	+0.02	0.05	2250	2942	8.95	10.05
P1-F4	21.6	21.0	2.80	2.82	+0.02	0.05	549	757	5.97	6.86
P2-F4	21.6	20.8	2.81	2.82	+0.01	0.04	492	471	5.04	3.65
P3-F4	21.6	20.8	2.78	2.82	+0.05	0.08	323	305	3.36	2.22
P4-F4	21.5	20.4	2.81	2.84	+0.17	+0.04	304	329	3.67	2.81
P5-F4	21.6	20.7	2.80	2.82	+0.19	+0.04	209	248	1.81	1.78
ZM1-F4	20.9	20.1	2.93	2.96	+0.10	0.26	1008	1000	2.51	6.06
ZM2-F4	23.3	22.5	2.95	2.99	+0.38	0.30	187	343	1.43	3.75
ZM3-F4	23.0	22.2	3.10	3.12	+0.21	0.17	479	994	2.70	6.40
ZM4-F4	23.3	22.9	3.16	3.22	+0.09	0.15	632	1577	4.51	4.07

(1) Shrinkage unless marked with a plus sign.

Table 4

Iron Oxide Bursting Characteristics of Fused Spinel Bodies Bearing Either Fused Periclase or Magnesia-Stabilized Zirconia

Body No.	Composition	Maturing Temperature 2700°F.	2910°F.
O-F4	100% fused spinel	Extreme	Extreme
P1-F4	10% MgO	Extreme	Moderate to extreme
P2-F4	20% MgO	Moderate to extreme	Moderate
P3-F4	30% MgO	No test	No reaction
P4-F4	40% MgO	No reaction	No reaction
P5-F4	55% MgO	No reaction*	No reaction*
ZM1-F4	10% ZrO_2	Extreme	Extreme
ZM2-F4	20% ZrO_2	Extreme	Extreme
ZM3-F4	30% ZrO_2	No Test	Extreme
ZM4-F4	40% ZrO_2	No Test	Extreme

*Delayed cracking noted in these specimens after exposure to laboratory air for several weeks

somewhat unfavorably with 100% fused spinel bodies formulated from previous lots of material. The porosities are higher and the densities and strengths somewhat lower. A pronounced tendency, not previously observed, for some of the larger grains to disintegrate during the firing process was noted in the O-F4 specimens. This may possibly explain the lower cross breaking strengths.

IV. PROPERTIES OF FUSED SPINEL BODIES AS AFFECTED BY HEAT TREATMENT

Compositions

The effects of time and temperature of firing on the physical properties of two fused spinel bodies were investigated. Interest in such data has repeatedly been expressed by those refractory manufacturers who are cooperating in developing full scale pouring tubes for a plant trial.

Two bodies, O-F4 and MO-5F4, were used in this series of tests. A shortage of fused spinel from the same lot precluded the incorporation of more bodies in this study.

Body MO-5F4 is comprised of 45% coarse (-8+20), 15% intermediate (-20+65) and 35% fine (-65) fused spinel to which is added 5% lightly calcined magnesia and 3.85% of $MgCl_2 \cdot 6H_2O$ solution (sp. gr. 1.2 g/cc). As mixed, this body is suitable for pressing or ramming without adding any auxiliary agents. Three percent Carbowax 4000 was added to Body O-F4. (See Table 1 for composition and grain sizing.)

Ten 1-in. x 1-in. x 6-in. bars and one tube section 8 inches

high by 3 inches OD were formed from each individual mix. The bars were pressed and the tube sections were rammed. In all, 50 bars and 4 tube sections were prepared from each body. This provided enough specimens so that 10 bars and 1 tube of each body could be fired under four varying sets of conditions. The fifth set of bars from each mix was fired under still different conditions. All specific firing conditions are listed in the first column of Table 5.

Fired Properties

The physical property data summarized in Table 5 indicate that both bodies can be fired over a wide temperature range and for varying times without altering the physical properties to any great extent. One exception to this is the apparent permeability (Pa) which was measured using the tubular specimens.

The apparent permeability was measured with the apparatus (previously reported by Ohynsty) shown in Figure 2. Although this shows a 6-in. OD tube mounted for testing, the procedure was the same for the 3-in. OD tubes--nominal length 6 inches--which were used in this investigation.

The specimen is clamped to the lid, which is in turn bolted to the tank. Prior to mounting, both ends of the tube are coated with melted paraffin. When this has cooled, a closed pore, sponge rubber gasket is placed on both ends. Under the pressure applied by the clamping bolts, the paraffin and gasket deform to make an air-tight seal. This can be checked with a soap solution by pressurizing the center of the tube.

Table 5

The Effect of Time and Temperature on the Fired Properties of Fused Spinel Bodies O-F4 and MO-5F4

Firing Temp., °F.	Treatment Time, Hr.	Porosity, %	Density, g/cc	Linear Change, %	Modulus of Rupture, psi	Youngs Modulus psi (x 10^{-6})
		Body O-F4 (100% fused spinel)				
2600°	10	20.3	2.83	0.02	2786	9.74
2700°	10*	20.1	2.84	0.05	2880	10.4
2850°	5	19.6	2.86	0.04	3125	11.3
2850°	10	19.9	2.84	0.11	3055	12.0
3000°	10	19.4	2.86	0.07	3633	12.4
		Body MO-5F4 (5% magnesium oxychloride)				
2600°	10	18.6	2.91	0.00	906	6.98
2700°	10*	19.4	2.88	0.03	849	7.10
2850°	5	18.6	2.91	0.12	1222	7.87
2850°	10	19.5	2.87	+0.03	894	7.07
3000°	10	18.1	2.92	0.20	1382	8.97

*No tubes fired with the bars which provided this data

With the lid assembly bolted to the tank, air is then supplied through a drier-cleaner unit to two pressure regulators. Air under pressure is supplied to the center of the tube through polyethylene tubing. The air permeating the tube is then collected in the tank, passed through the flow meter, and exhausted to the atmosphere. The pressure difference between the input and outlet pressures is read on the manometer. The desired constant pressure difference and steady flow are attained before results are recorded.

The apparent permeability was calculated from:

$$Pa = \frac{Vd}{At}, \frac{cm^3 \times cm}{cm^2 \times sec}$$

where V = volume of air in cc flowing in t seconds

d = average wall thickness in cm

t = time of flow in seconds

A = logarithmic mean surface of the tube section

$$A = \frac{A_2 - A_1}{2.3 \log (A_2/A_1)}$$

and A_2 = outside surface area in sq. cm.

A_1 = inside surface area in sq. cm.

The data obtained from studying the effect of time and temperature on the apparent permeability of bodies O-F4 and MO-5F4 are plotted in Figures 3 and 4. The data from a section of an alumino-silicate tube prepared by Electro Refractories are also plotted for comparative purposes.

In general, these studies show the following:

1. There was no systematic change in the apparent

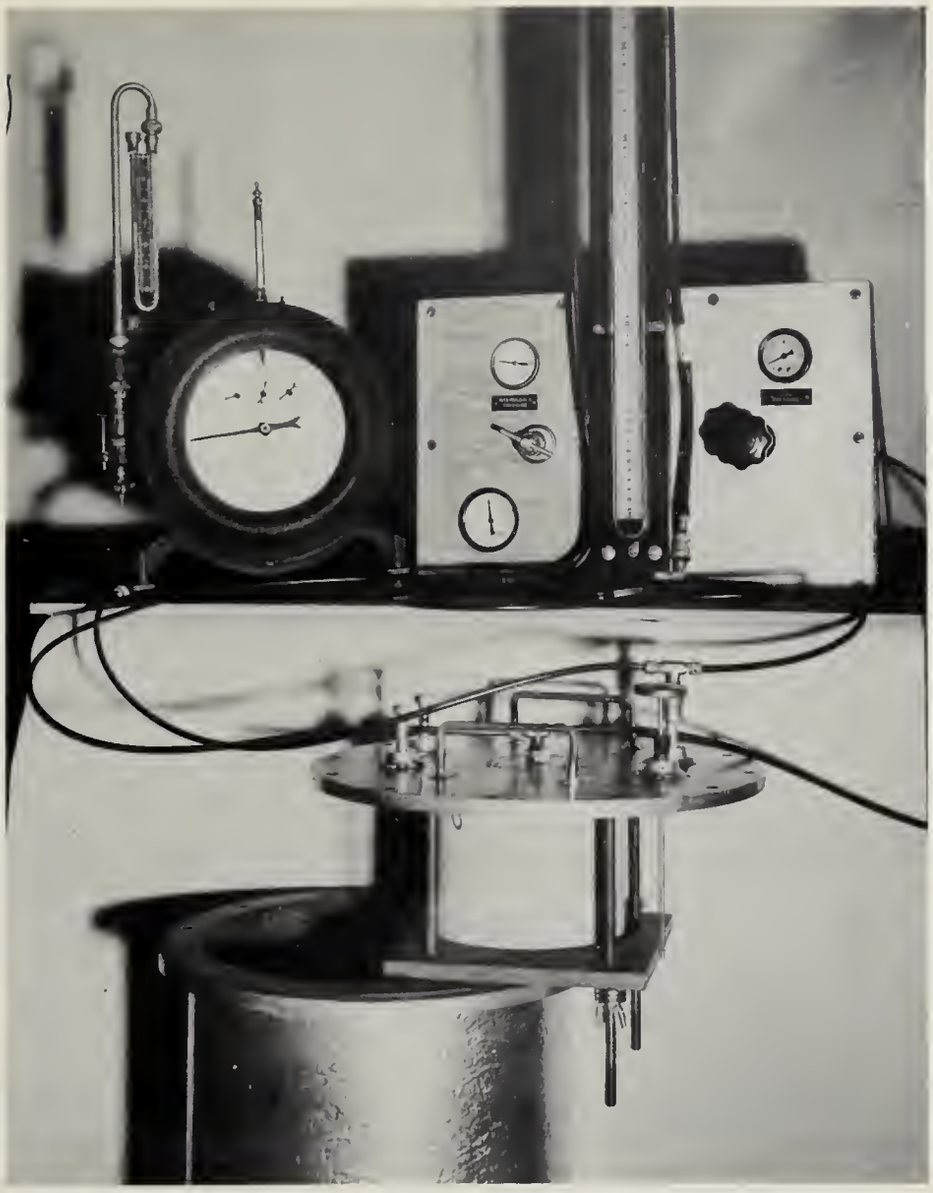


Fig. 2. Permeability Apparatus Showing Tank (center bottom), Lid and Specimen (on tank edge), Flow Meter (upper left) and Pressure Regulators (upper right).

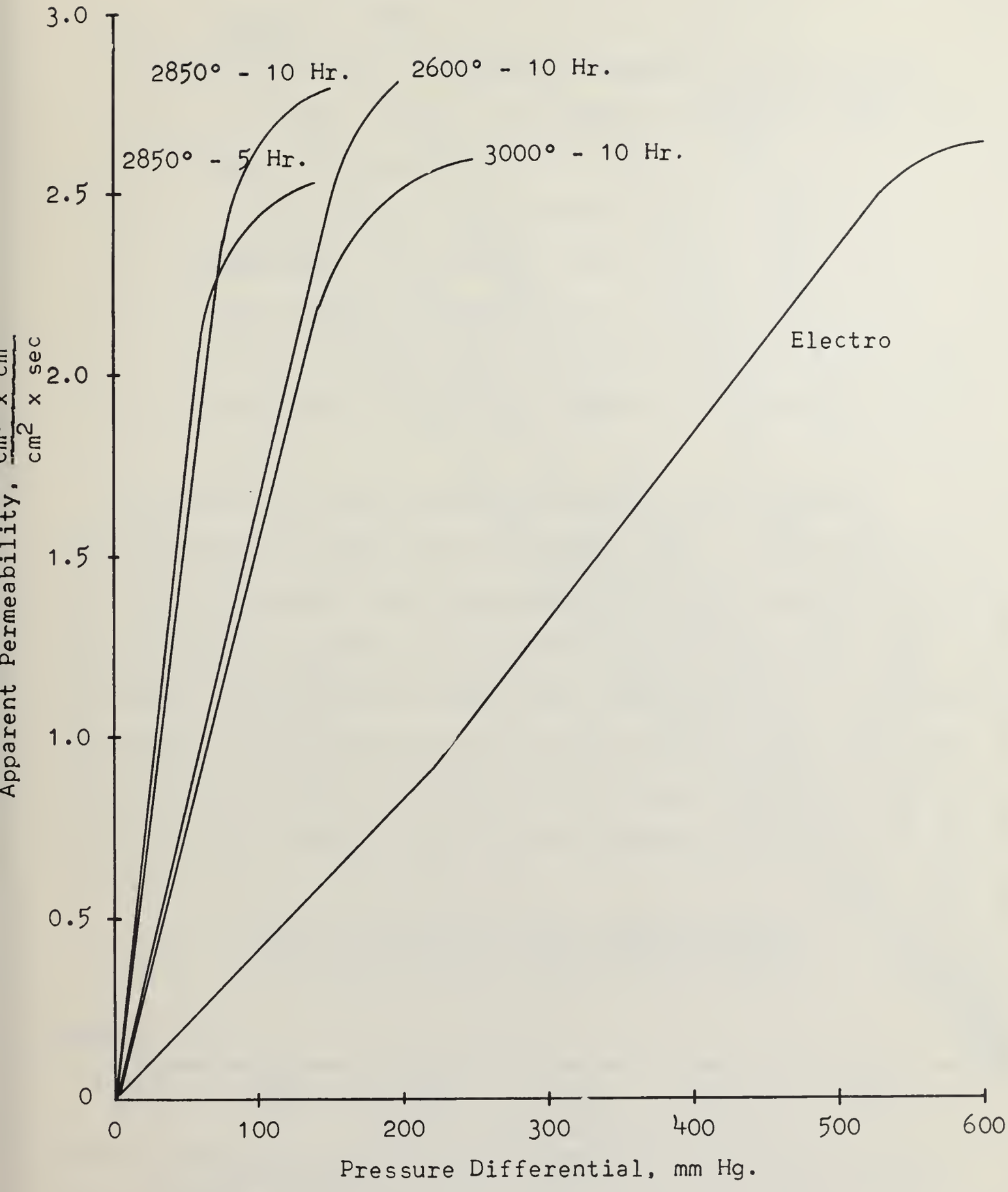


Fig. 3. The Effect of Firing Time and Temperature on the Apparent Permeability of Body O-F4

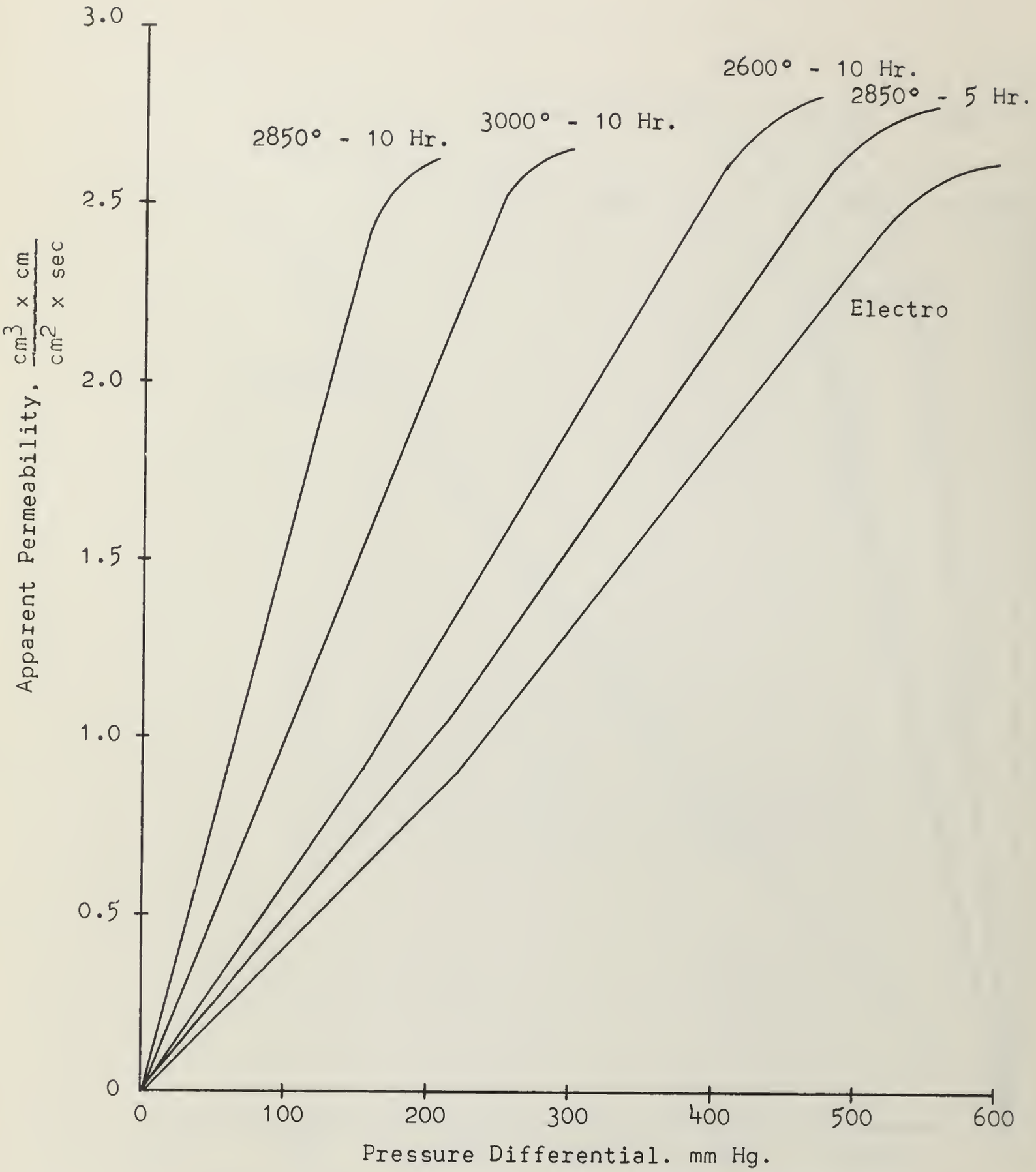


Fig. 4. The Effect of Firing Time and Temperature on the Apparent Permeability of Body MO-5F4

permeability of either body as a result of changes in firing temperature or firing time.

2. The apparent permeability of Body MO-5F4 was lower than that of Body O-F4 for every condition of firing time and temperature.

3. It is possible, as evidenced by the results with body MO-5F4, to produce fused spinel bodies which have apparent permeabilities close to that of the Electro fireclay body. Apparently these bodies also represent the optimum conditions of ramming procedure.

The absence of any systematic change in the apparent permeability with temperature for either type of body may indicate that the results were more dependent on structural variations from specimen to specimen than on the firing conditions. The individual specimens were formed from separate batches, and minor variations in water content or in mixing may be responsible for slight, but important, structural differences. Breakdown of particles during ramming might also be responsible.

V. EFFECT OF PARTICLE SIZE DISTRIBUTION ON THE PROPERTIES OF FUSED SPINEL BODIES

Compositions

In general, the previous study indicated that the optimum firing temperature, in so far as permeability was concerned, seemed to be in the range of 2850°F. No regular pattern was noted for the data, and it appeared that certain optimum

conditions of forming and firing were required to produce permeabilities approaching that of the Electro fireclay body.

To insure an adequate supply of material for the complete particle size study, a new 200 lb. lot (No. 5) of fused spinel was purchased. This was separated into the usual size fractions. However, prior to this, the material was annealed by firing it at 1800°F. for several hours and then slow cooling in the furnace. The purpose of this was twofold: (1) to eliminate residual electrode carbon, and (2) to eliminate, if possible, the tendency previously noted (Section III) for the larger grains to disintegrate when fired.

To test the effectiveness of this procedure, and to compare the fired properties of a body prepared from this lot with those from previous lots, twenty 1-in. bars of Body O-F5 were tested according to the oft used procedure which involves initial firing at 2700°F. and reheating at 2910°F. No tendency for the large grains to disintegrate was noted. The physical properties of Body O-F5 such as porosity, density, and fired strength were superior to Body O-F4 tested by the same procedure.

The bodies formulated to study the effect of particle size are listed in Table 6. Numbers I and VIII were the control bodies and correspond, according to previously used body designations, to O-F5 and MO-5F5, respectively. Roman numeral designations for this series of bodies were adopted to eliminate more cumbersome body numbers.

Two relatively unusual body compositions appear in Table 6. Numbers IA and IB contained 2% of the gross weight of the batch

Table 6

Variations of Bodies O-F5 (100% Fused Spinel) and MO-5F5 (5% Magnesium Oxychloride) Used to Study the Effect of Particle Size Distribution on the Physical Properties

Per Cent by Weight

Body No.	Fused Spinel Grain -8 +20 mesh	-20 +65 mesh	-65 mesh	Sintered Spinel -65 mesh	Magnesium Oxide	Gradation No. -65 mesh Fraction	Additives
I	45	15	40	--	--	1	--
IA	45	15	40	--	--	1	2% Al(1)
IB	45	15	40	--	--	1	2% Ti(1)
IC	45	15	40	--	--	1	2% TiO_2(1)
II	45	7.5	47.5	--	--	1	--
III	45	--	55	--	--	1	--
IV	35	15	50	--	--	1	--
V	45	15	40	--	--	2	--
VI	45	15	--	40	--	3	--
VII	45	15	--	40	--	3	1% TiO_2(2)
VIII	45	15	35	--	5	1	$MgCl_2 \cdot 6H_2O$(3)
IX	45	7.5	42.5	--	5	1	"
X	45	--	50	--	5	1	"
XI	35	15	45	--	5	1	"
XII	45	15	35	--	5	2	"
XIII	45	15	--	35	5	3	"
XIV	45	15	--	35	5	3	1% TiO_2(2) $MgCl_2 \cdot 6H_2O$(3)

(1) As per cent of gross batch

(2) As per cent of sintered spinel only

(3) 3.85% of solution with sq. gr. of 1.2 g/cc

Per Cent Retained

Gradation No.	-65 +100	-100 +200	+200 +270	-270
1 (Fused)	8.4	15.2	9.4	67.0
2 (Fused)	99.7% finer than 325 mesh			
3 (Sintered)	8.3	14.8	10.1	66.7

as either very finely divided aluminum or titanium powders. These additives were cued by a procedure sometimes used in sintered alumina bodies whereby metallic aluminum additions are used to increase the densification of the fired pieces.

All bodies were processed according to the procedures previously outlined. Ten 1-in. x 1-in. x 6-in. bars were pressed for each mix, and one 3-in. OD x 1½-in. ID cylinder approximately 8 inches long was rammed. Bodies I through VII contained 3% Carbowax 4000 as a temporary binder. All specimens were fired for five hours at 2800°F.

Fired Properties

The physical property data obtained are summarized in Table 7. Unfired densities were computed from appropriate physical measurements of the bar specimens. This property was determined to note if any close correlations between green and fired densities existed.

In spite of the wide variation of particle sizing represented in the bodies listed in Table 7, only minor variations in properties occurred. Surprisingly enough, all 17 bodies developed mechanical properties which are considered to be satisfactory. The permeability, therefore, appears to be the most critical property for evaluating such mixes.

The addition of 2% titanium to Body I (O-F5) was quite effective as a densifying agent. The only property of this body which was adversely affected was the cross breaking strength; this was decreased radically. Moderate to bad warpage in some

Table 7

Physical Properties of Fused Spinel Bodies Used in the Study of the Effect of Particle Size Distribution (Firing conditions: 5 hr. at 2800°F.)

Body No.	Bulk Density, g/cc Green	Bulk Density, g/cc Fired	Apparent Porosity, %	Linear Change, %	Modulus of Rupture, psi	Young's Modulus psi (x10-6)
I	2.91	2.86	19.5	-0.08	2377	9.55
IA	2.89	2.87	19.1	-0.08	2045	8.39
IB	2.89	2.91	18.1	-0.43	965	13.55
IC	2.92	2.87	19.2	-0.34	3065	13.87
II	2.88	2.84	19.9	-0.15	2512	9.75
III	2.84	2.81	20.7	-0.23	2617	10.15
IV	2.87	2.82	20.6	-0.22	2916	10.62
V	2.87	2.85	19.8	-0.31	1633	7.40
VI	2.89	2.86	19.6	-0.32	1562	7.81
VII	2.88	2.87	19.3	-0.37	1746	8.59
VIII	2.95	2.89	18.9	+0.03	1017	6.44
IX	2.92	2.89	19.2	-0.06	1392	7.52
X	2.89	2.86	19.7	-0.13	1453	7.73
XI	2.92	2.88	19.1	-0.08	1564	8.52
XII	2.91	2.88	19.2	-0.14	1056	5.78
XIII	2.86	2.87	19.5	-0.04	1000	5.90
XIV	2.94	2.90	18.7	+0.03	1196	6.57

Note: Specimens of Body V were slightly to moderately surface checked after firing, while those of Body XII were badly surface checked.

specimens of this body was noted.

Titanium dioxide added as 2% by weight of the gross batch (as in Body IC) was much more effective as a sintering aid than elemental titanium. Two per cent titanium has a TiO_2 equivalent of about 3.3%. Considering that most of this element must have been oxidized during the firing, it is surprising that the two materials did not produce more nearly the same results. Two factors may have had some bearing: (1) the Ti was not completely oxidized; and (2) the oxidation process occurred at the critical time in the sintering process and, therefore, exerted little or no effect.

The substitution of extremely fine -65 mesh spinel for a more normal sizing (compare Bodies I and V, also VII with XII) apparently produced matrixes which were more prone to shrink away from the larger grains. This observation is based on the surface checking noted in both Bodies V and XII. That the checking was more pronounced in Body XII as compared to V is explainable on the basis that an additional 5% of very fine material as MgO was present in Body XII.

The substitution of sintered spinel for fused spinel in the -65 mesh fraction had a deleterious effect on the fired strength, while the other properties were not changed. This effect has also been noted in work previously reported. Combinations of sintered spinel and TiO_2 in the fine fraction showed less adverse effect than when sintered spinel was used alone. Or, by the opposite interpretation, TiO_2 in this small amount has beneficial effects but not sufficiently so to overcome the adverse effect

of substituting sintered fines for fused fines.

The permeability data obtained are plotted in Figures 5 and 6. Body IB was not tested.

While many of the grain size modifications of Body O-F5 (Figure 5) had some beneficial effects in lowering the permeability, these effects were not sufficient to produce values approaching that of the referee material.

Data previously presented in Section IV have shown that under optimum conditions the permeability of 100% fused spinel bodies can approach that of the Electro composition. The precise factors which must be controlled to accomplish this consistently are not known. It is suspected that variables encountered in the ramming process are the controlling factors. The amount of water used in Bodies I through VII had to be adjusted, based on the operator's judgment, to produce mixes which would ram well. Changing the particle sizing and maintaining a standard water content produced bodies in some cases which were too wet. Therefore, change in the water content was an unavoidable variable.

The data plotted in Figure 6 show that the magnesium oxychloride bonded body, MO-5F5, has inherently lower permeability than Body O-F5. This cannot be a simple function of the added fineness in the -65 mesh fraction due to the substitution of MgO for spinel because using extremely fine -65 mesh material (as in Body VII) had a deleterious effect on the permeability.

It is obvious from Figure 6 that some fairly radical changes in the sizing of Body MO-5F5 can be made without altering the permeability to any great extent. These modifications also

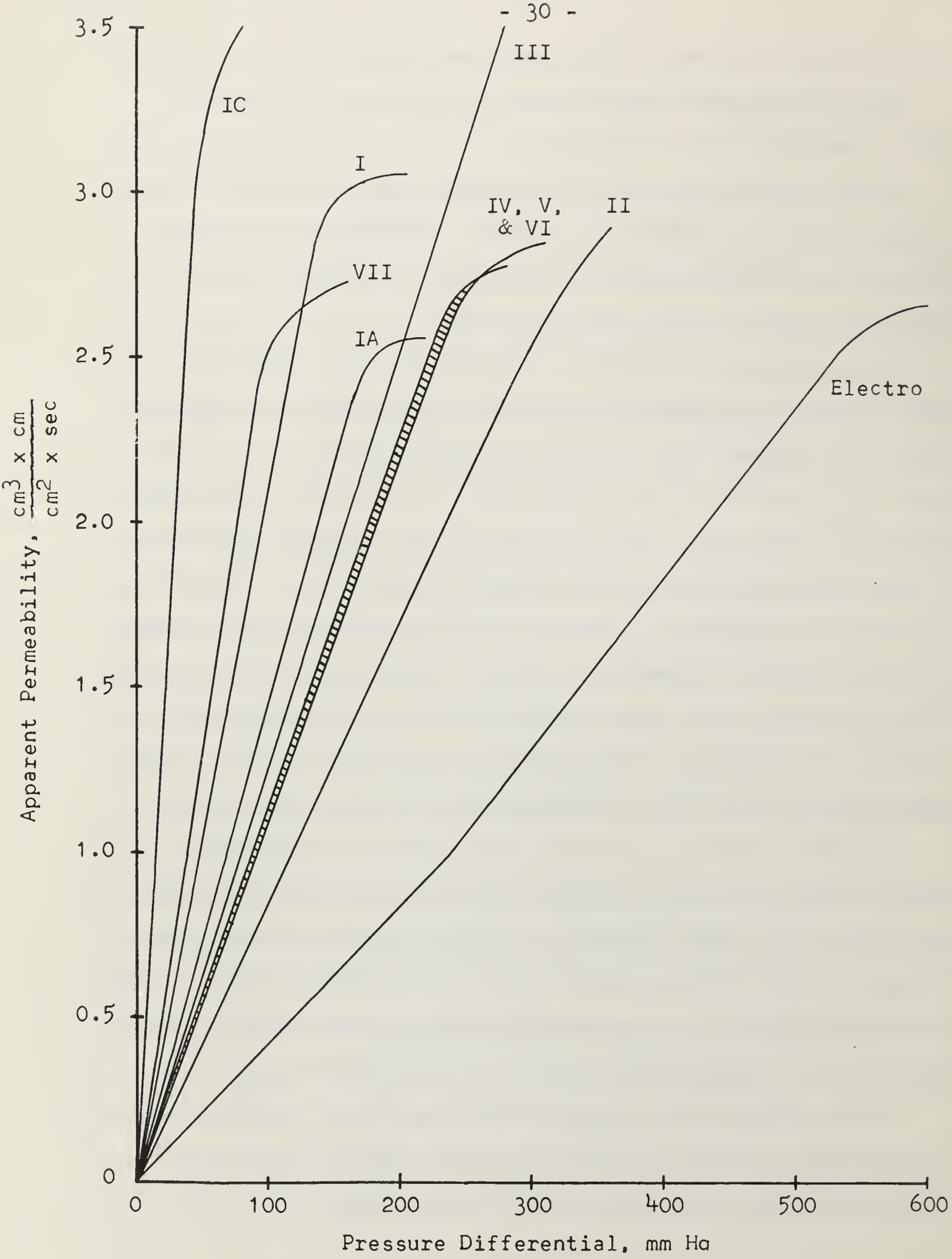


Fig. 5. Apparent Permeabilities of Modifications of Body O-F5.

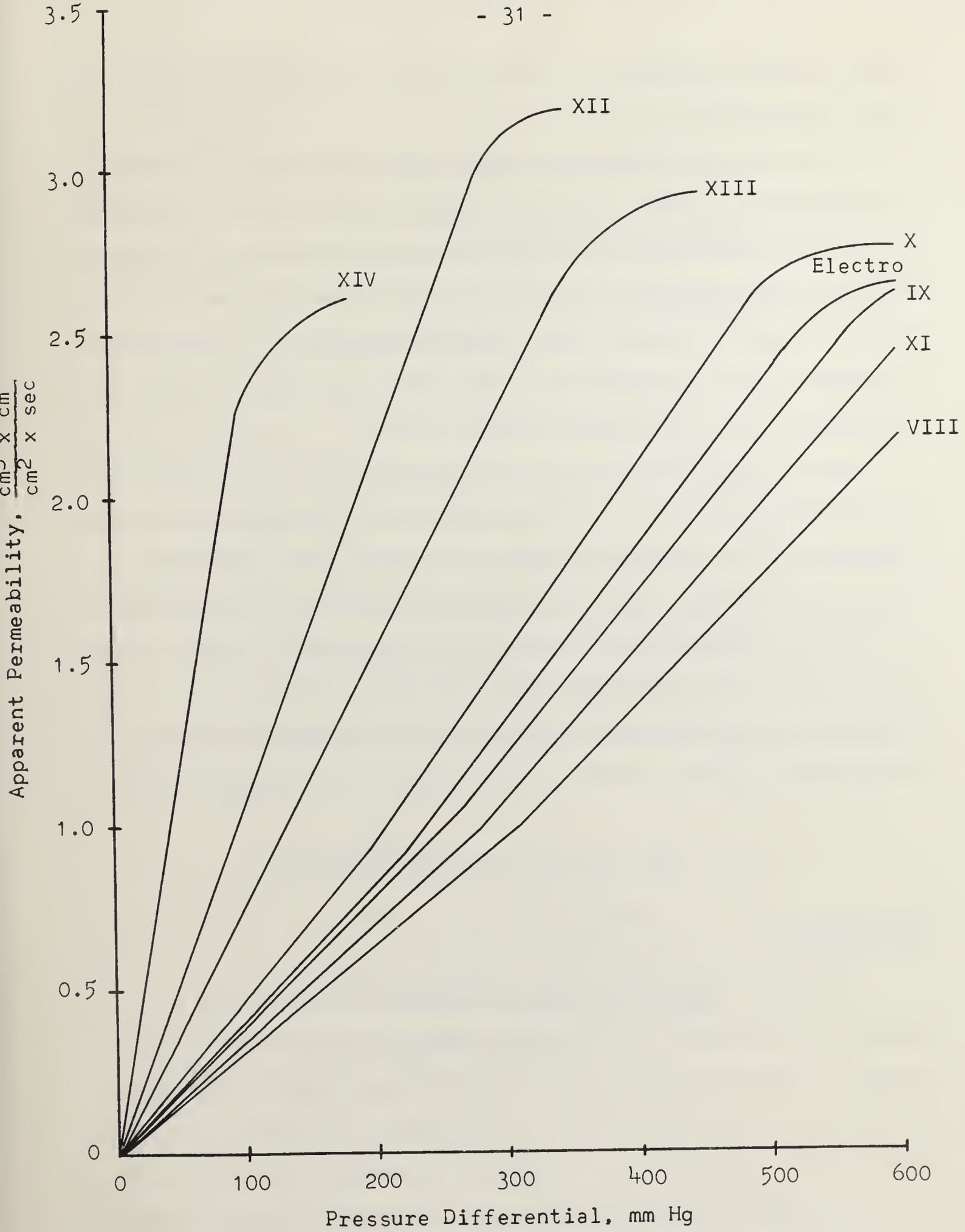


Fig. 6. Apparent Permeabilities of Modifications of Body MO-5F5

compare quite favorably with the Electro tube composition in their permeability.

This group of bodies was rammed from mixes which contained a standard $MgCl_2 \cdot 6H_2O$ solution addition. Due to the consistency of the solution, changes in the total surface area due to variations in the amounts of the various size fractions used had little apparent effect on the ramming consistency. This particular body, in all its modifications, seems to be well suited to fabrication by the ramming process.

As a control measure, the fired densities of all tubes used for permeability tests were determined and compared with the bar densities of the respective mixes. In every case, the tube densities were higher. This value ranged between 2.89 to 2.97 g/cc for the O-F5 from 2.94 to 3.11 g/cc for the MO-5F5 group. It is typical that the rammed densities are higher than the densities of pressed specimens, and also that the magnesium oxychloride bonded material is more dense than straight spinel.

VI. RING SECTION DEFORMATION STUDIES

Introduction

At normal temperatures brittle materials are highly sensitive to stress concentration resulting in difficulty in the design of specimens and in the design and alignment of sample fixtures to test such materials. At elevated temperatures these difficulties are increased. If the holders are outside of the furnace, sample design is complicated by such factors as length,

alignment, and temperature gradients. If the holders are within the furnace, they must be constructed of materials that are not affected at the testing temperature. In addition, long uniaxial spans must be maintained because of furnace space requirements and the testing machine must be protected from heat.

A method has been suggested by M. M. Frocht[1] which minimizes or eliminates such problems. This test consists of placing a ring section under diametral compressive loading, which results in the development of maximum tensile stresses on the inside circumference in the loading plane. Tension, to a lesser degree, is also developed on the outside circumference in a plane perpendicular to the loading plane. Compressive stresses are developed on the opposite sides of the neutral axes of these same points; however, these stresses may be neglected since failure will normally be caused by the maximum tensile stress.

Frocht[1] has developed an empirical equation for determining the failure stress in a ring,

$$S = \frac{pK}{(D - Zr)t}$$

where S = ultimate tensile strength

K = stress constant dependent on the ratio of the inside to outside diameter

p = the breaking load

D = outside diameter

2r = inside diameter

t = width of the sample

The following procedure was employed by Bortz and Lund[2]

to experimentally verify the stress constants for different materials. Electrical strain gages were attached on the inner radius where the line of load cuts the inner circle at both top and bottom. The gages were placed so that they would record the strain perpendicular to the direction of the load forces. Tensile strength were calculated from the measured strain and the elastic modulus of the material using the formula,

$$S = Ee$$

where S = tensile stress

E = Young's elastic modulus of the material

e = the measured strain

Results of calculation for stress constants from strain gage data when compared to calculated theoretical values show excellent correlation.[2]

The ring technique can be very helpful in the study of brittle materials at ambient and even more so at elevated temperatures. The need for sample holders and sample alignment is eliminated. The sample aligns itself between two parallel planes and the procedure employs compression as a means of obtaining tensile stress. This technique has been utilized by Bortz and Lund[2] to determine the tensile strength of brittle materials such as concrete, acrylic plastic, gypsum cement, graphite, porcelain, alumina, steatite, and cordierite. Rippenger and Davis[3] have utilized this same method to determine the tensile strengths of stone and concrete.

The method appears to have a natural application to the study of refractories for pouring tube use since test specimens

may be made by simply cutting ring sections from actual production pieces.

Although this method has been used by several investigators to determine the tensile strengths of various materials, there are no instances in which it has been utilized for the determination of deformation under load at elevated temperatures.

A study of the applicability of this method at elevated temperatures was undertaken.

Apparatus and Procedure

The apparatus consists of a Globar furnace so constructed that two rings of 3-inch outside diameter may be loaded in compression simultaneously. Loading is accomplished by vertical extension rods which extend through the furnace roof to the top of the ring specimen. Ports in the side of the furnace permit visual observation of the horizontal and vertical deflection of the specimen. Two sets of telescopes mounted in micrometer slides have been installed for this purpose.

The furnace is brought up to the test temperature over a 20-hour interval by means of a manually controlled variable transformer. When the desired temperature is attained, the furnace is controlled by an on-off controller.

Preliminary trials were made to determine the load required to give a measurable deformation over a reasonable time interval at a test temperature of 1300°C. The samples used had the following approximate dimensions: inside diameter, 1.4 inches; outside diameter, 3.0 inches; thickness, 1.25 inches. They were cut from

rammed tubes prepared in this laboratory.

Results

Several trials to determine the applicability of this method to the study of the deformation characteristics of refractories for pouring tube use were made.

The results of one of these trials on ring sections cut from a tube section which had been fired at 2850°F. for five hours are included in Tables 8 and 9. Samples A and C were run simultaneously, as were B and D. The horizontal and vertical dimensional change versus time is reported as percent of the original dimension.

The time required for rupture to occur is included for each sample. The total load in all cases was 22 pounds. This corresponds to approximately 70 psi tensile stress when calculated according to the method outlined by Frocht.[1] This stress level is higher than used in the conventional compressive load test (usually 25 or 50 psi). It represents, therefore, not only a stress condition which is extreme, but also a stress level which is greater than normally used in testing. This larger load was selected in an attempt to get measureable deformations in a reasonable length of time.

As seen from Table 8, there is no apparent correlation between the change in the horizontal and vertical dimension of Sample A. The same may be said of sample B.

A comparison of the changes in the vertical dimension of samples B and D, which were run simultaneously, shows no

Table 8

Percent Deformation as Function of Time and Temperature for Samples A and C

Elapsed Time Hours	Temperature °C.	Sample A Horizontal	Sample A Vertical	Sample C Vertical
2.5	400			
12.5	820	0.102	0.092	-0.294
15.8	1090	0.752	-0.418	-0.299
19.0	1216	0.819	0.217	-0.010
20.0	1235	0.529	-0.292	-0.971
21.0	1290	0.535	0.217	-0.644
21.1 (3)	1300	--	--	--
24.0	1300	0.589	-0.021	-0.879
28.0	1300	-- (1)	--	-0.781
36.5	1300			-1.440
38.5	1300			-1.485
39.3	1300			-(2)-

(1) Sample A ruptured between 24.0 and 28.0 hours elapsed time

(2) Sample C ruptured at 39.3 hours elapsed time

(3) Test temperature of 1300°C. was attained in 21.1 hours

(-) Denotes percent decrease of original dimension

Table 9

Percent Deformation as a Function of Time and Temperature for Samples B and D

Elapsed Time Hours	Temperature °C.	Sample B Horizontal	Sample B Vertical	Sample D Vertical
16.8	1180	0.664	0.521	0.351
18.3	1240	0.492	0.477	0.621
19.0	1280	1.162	-0.260	0.257
20.3 (3)	1300	--	--	--
20.4	1300	1.128	0.809	0.501
22.5	1300	1.105	0.774	0.775
23.8	1300	1.005	0.776	0.399
26.5	1300	1.173	0.881	0.105
35.0	1300	1.273	0.789	0.076
35.5	1300	1.434	0.752	-(2)-
37.5	1300	3.434	0.916	
38.0	1300	1.435	-0.292	
40.0	1300	1.602	0.477	
43.7	1300	1.484	-0.035	
46.0	1300	1.515	-0.048	
47.7	1300	-- (1)	--	

(1) Sample B ruptured at 47.7 hours elapsed time

(2) Sample D ruptured between 35.0 and 35.5 hours elapsed time

(3) Test temperature of 1300° was attained in 21.3 hours

(-) Denotes percent decrease of original dimension

correspondence. The same is true for samples A and C.

In addition the time-to-rupture in each case varied considerably. (See footnotes, Tables 8 and 9).

The greatest source of error in this method apparently is due to the rotation and shifting of the sample during the test. Because of this the plane defined by the horizontal and vertical diameters of the specimen does not remain perpendicular to the line of sight, thus resulting in erroneous values of dimensional change. The relatively high value of tensile stress used in the experiment may also have caused an anomolous variation in the mode of fracture.

A more satisfactory test may result if the hot strength of ring sections is determined by this method in which preheated specimens are loaded at a controlled rate to failure. This procedure would allow: (1) data on hot tensile strength to be computed by the method of Frocht; and (2) a greater number of samples to be treated in a statistical manner. Plans to develop this information are in progress.

It will also be necessary to establish more conventional compression load test data as part of the property evaluation in this study.

VII. ALUMINUM TITANATE

In contemplating refractory materials other than magnesium aluminate for use in the pressure pouring process, aluminum titanate was considered to have properties which justified some probing studies.

The mechanical properties of aluminum titanate as produced by sintering were known to Project personnel from work on other research projects. These were not considered adequate. However, it was thought that electrically fused aluminum titanate might have improved properties. Therefore, an agreement was reached with Muscle Shoals Electrochemical Corporation to make some trial fusions.

Only one sample was received. This proved to be well developed aluminum titanate with a slight excess of TiO_2. On reheating at 2175°F., this dissociated into alpha alumina and titania, as rutile.

The hand sample was quite porous and somewhat weak structurally. Thus, as a refractory grain source, it did not appear too promising. In view of the chemical instability of the material, the structural properties were of secondary importance.

Therefore, it was requested that two additional fusions be made in which magnesia, reported to be a stabilizing agent, was to be incorporated. It was reasoned that a stable compound should be developed before attempting to improve the structural properties of the "pig" by modifying the fusion process.

No magnesia-bearing samples were ever received. A reorganization of the management at Muscle Shoals Electrochemical Corporation, with some losses in operating personnel, forced a shut down of their ceramic production. Inasmuch as sample delivery could not be assured before February 1960, the purchase order with this company for aluminum titanate samples was canceled.

While another company was located which would make, as a

cooperative venture, small scale fusions on a custom basis, this probing investigation was not reactivated.

VIII. SERVICE PROJECTS

Some service projects were undertaken during the contract period. These fell into four categories: (1) plant visitations by Project personnel and meetings held at Urbana to discuss with potential fabricators the research relative to magnesium aluminate; (2) thermal expansion studies; (3) particle size determinations of mold wash materials; and (4) testing of small pouring tubes submitted by Electro Refractories.

Three formal meetings of one day's duration were held in the Department of Ceramic Engineering to present the results of the research with spinel and to discuss the problem of producing full size tubes for plant trials.

Personnel from Electro Refractories and Abrasives Corporation and the Babcock and Wilcox Company attended separate meetings during the spring semester. Members of the A. P. Green Fire Brick Company were present at a similar meeting in September. Arrangements were made at this time to purchase 1000 lb. of A. P. Green's sintered spinel. This was delivered January 11, 1961.

Project personnel visited sea water magnesia plants of the Michigan Chemical Company at Port St. Joe, Florida and St. Louis, Michigan during during Feburary 1960. This category of material is a potentially economical source of high purity MgO. An account of this trip was given in Report No. 13.

The facilities for the production of fused spinel at the

Muscle Shoals Electrochemical Corporation, Tuscumbia, Alabama were inspected in June 1960. A detailed report of this visit, and of a visit to the Refractories Research Laboratories of Babcock and Wilcox, Augusta, Georgia to discuss problems involved in the fabrication of 6-foot fused spinel tubes was submitted to Mr. Woodburn July 11, 1960.

In January of 1961, Project members met with A. P. Green research personnel at Mexico, Missouri to discuss the potential of sintered magnesium aluminate in the development of refractories for the pressure pouring process.

The thermal expansions of two German pouring tubes and one from General Refractories were determined by the dilatometer method. These data were presented in Report No. 14.

Particle size determinations by Andreasen pipette were made on two samples of "Glasrock" fused silica. These results were submitted in Report No. 14.

Report No. 15 contained the results obtained from some tests conducted on small spinel tubes (3-in. OD) submitted by Electro Refractories and Abrasives Corporation, Buffalo, New York. A copy of the section of the report pertaining to these tests was sent to Mr. George Easter of that company.

IX. REFERENCES

1. Frocht, M. M., Strength of Materials, Ronald Press, New York, 1951.

2. Bortz, S. A. and Lund, H. H., "The Brittle Ring Test," Presented at Conference on Mechanical Properties of Engineering Ceramics; March 9, 10, 11, 1960, North Carolina State College; Raleigh, North Carolina.

3. Rippenger, E. A. and Davids, N., "Critical Stresses in a Circular Ring," Transactions of American Society of Civil Engineers, Paper No. 2308, Volume 73 (1947).

UNIVERSITY OF ILLINOIS-URBANA
669.8W682S C001 V002
SUMMARY REPORT ON FUNDAMENTAL STUDY OF P
3 0112 008828912